Soft Science

Review Article

Polyelectrolyte-based conductive hydrogels: from theory to applications

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Abstract

With the continuous development of soft conductive materials, polyelectrolyte-based conductive hydrogels have gradually become a major research hotspot because of their strong application potential. This review first considers the basic conductive theory of hydrogels, which can be divided into the hydrogel structure and zwitterionic enhancing conductivity theories. We then classify polyelectrolyte-based conductive hydrogels into different types, including double, ionic-hydrogen bond, hydrogen bond and physically crosslinked networks. Furthermore, the mechanical, electrical, and self-healing properties and fatigue and temperature interference resistance of polyelectrolyte-based conductive hydrogels are described in detail. We then discuss their versatile applications in strain sensors, solid-state supercapacitors, visual displays, wound dressings, and drug delivery. Finally, we offer perspectives on future research trends for polyelectrolyte-based conductive hydrogels.

Keywords: Polyelectrolytes, hydrogels, flexible sensors, hydrogel sensors

INTRODUCTION

Conductive hydrogels are polymer mixtures or networks that combine intrinsically conductive electroactive polymers with highly hydrated hydrogels and represent a new category of multifunctional intelligent materials. These materials can combine the inherent properties of their constituent materials in order to obtain better application value than the original materials[1]. According to the different conductive materials,

conductive hydrogels can be classified into five categories, namely, conductive polymer-, carbon-, MXene-, metal-, and electrolyte/polyelectrolyte-based conductive hydrogels[2].

Conductive polymer-based hydrogels combine intrinsically conductive polymers to achieve conductive properties. However, researchers found that the conductivity of these hydrogels is usually limited by the separate islands of conducting polymers dispersed in the porous hydrogel matrix. As a result, the selection of conductive polymer raw materials and dopants/crosslinking agents is chosen to ensure that controllable electronic conductivity is achieved[3,4]. To produce hydrogels with better conductivity, carbon-based materials, such as carbon nanotubes and graphene, which have high conductivity, good environmental stability, and high mechanical strength, are used as conductive fillers in conductive hydrogels[5]. However, it was found that carbon materials are difficult to directly integrate into hydrophilic hydrogels because of their inherent hydrophobicity and poor solubility. To solve this problem, cellulose nanofibers and hydrophilic polymers are usually used to increase their hydrogel compatibility[6,7]. In addition to using one-dimensional and two-dimensional carbon materials as conductive fillers of conductive hydrogels, another successful attempt is to use two-dimensional transition metal carbides and carbonitrides, which are also known as MXenes. Using MXenes as conductive fillers or skeletons of hydrogels can endow hydrogels with good dispersibility and excellent mechanical properties[8,9]. As a result, there is significant potential in their practical applications. However, the preparation process and manufacturing cost of MXene-based hydrogels are more complex and expensive than others, so related research and applications currently remain at the laboratory stage. Metal-based conductive materials, such as gold and silver nanoparticles, have also been used in the preparation of conductive gels, especially aerogels. However, similar to carbon-based conductive hydrogels, metal particles are easily deposited in a polymer matrix, which affects the conductive and mechanical properties of hydrogels[5,6].

To solve these defects, conductive hydrogels based on polyelectrolytes have been prepared. In polyelectrolyte-based conductive hydrogels, the polymer backbone forms ionic bonds between positive and negative charges[10] and the three-dimensional frame structure of the hydrogel allows ions to move and transport freely, which gives the hydrogel excellent electrical conductivity[11]. Simultaneously, because there is no dark hydrophobic electronic conductive material in these hydrogels, the shape is more transparent and attractive than the previous gels and the cost and workmanship are cheaper and simpler, respectively[2]. In addition, polyelectrolyte-based hydrogels can show excellent fatigue resistance and mechanical properties by changing the percentage of positive and negative charge groups in the network structure. These properties mean that polyelectrolyte-based conductive hydrogels have the potential to be used in strain sensors, solid-state supercapacitors, visual display materials, wound dressing, and drug microspheres[12-16]. In recent years, the rapid development and excellent properties of polyelectrolyte-based hydrogels have attracted wide attention. Several reviews have been published on the preparation and application of hydrogels, with particular focus given to the preparation of hydrogels with biological tissue substitution, biocompatibility, and microsphere drug release[16-18]. However, their applications as conductive hydrogels have rarely been systematically reviewed according to their mechanism of action and mechanical properties.

In this review, we summarize the development process of polyelectrolyte-based conductive hydrogels in recent years regarding the theory and their types, properties, and applications. Finally, we propose suggestions for the future of polyelectrolyte-based conductive hydrogels based on the existing challenges. The purpose of this review is to promote our understanding of the conduction theory of polyelectrolyte-based conductive hydrogels and their network structures and their broad prospects in the areas of strain sensors, visual displays, and other fields, and illustrate their development and applications in recent years.
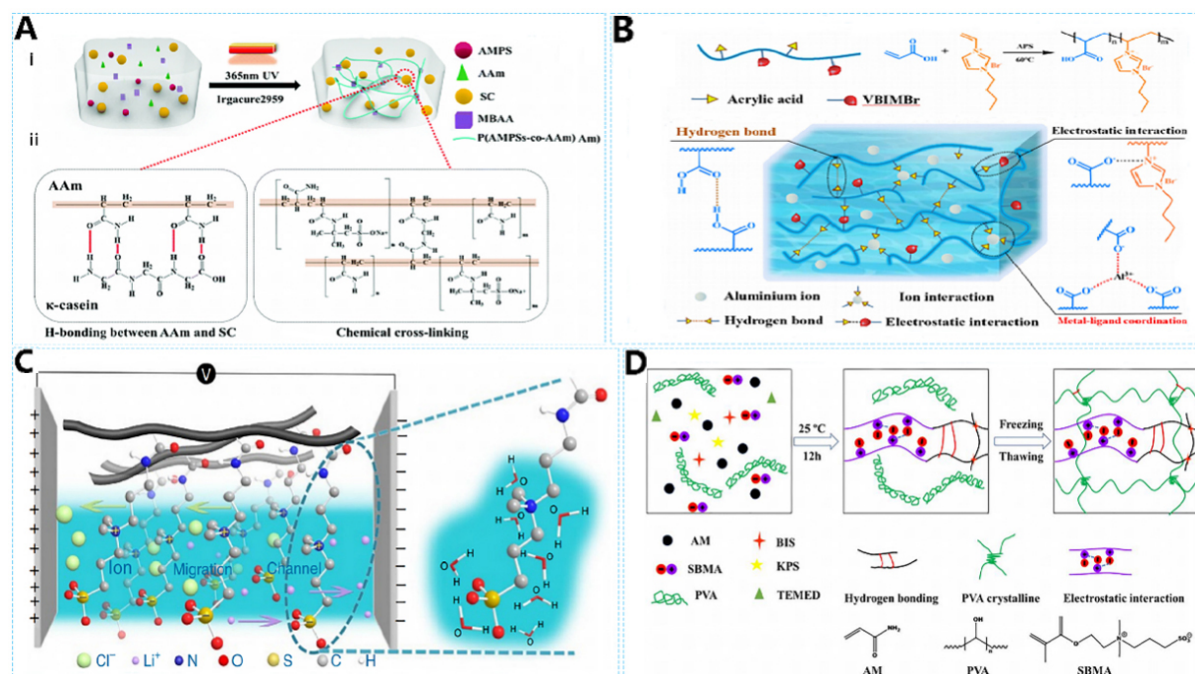
Figure 1. Conduction theory of polyelectrolyte-based conductive hydrogels. (A) Schematic illustration of the preparation and formation mechanism of P(AMPSs-co-AAm)/SC hydrogel and the reversible physical interactions between its components[23]. (B) Synthesis mechanism of AAV hydrogel[24]. (C) Schematic illustration of PPDP gel electrolyte applied on electrodes. The ion migration channel is formed by applying an external electric field. PPDP is strongly hydrated by water molecules with robust water retention ability due to the electrostatic interactions between the zwitterionic groups and water molecules[27]. (D) Schematic of fabrication of PVA/P(AM-co-SBMA) DN gels[28]. (A) Reproduced with permission[23]. Copyright 2021, RSC. (B) Reproduced with permission[24]. Copyright 2022, Elsevier. (C) Reproduced with permission[27]. Copyright 2016, Springer. (D) Reproduced with permission[28]. Copyright 2019, Wiley.

CONDUCTION THEORY OF POLYELECTROLYTE-BASED CONDUCTIVE HYDROGELS

Polyelectrolyte-based conductive hydrogels are generally composed of polymeric organic compound hydrogels, such as polyacrylate, which are used as the main structures, and ionic salts, such as lithium chloride (LiCl), which are used as conductive electrolytes[19-21].

For most polyelectrolyte-based conductive hydrogels, conductivity comes from the structure and the ions among the structure. The unique three-dimensional framework structure of hydrogels provides sufficient channels for ion migration and their porous networks allow water and small molecular solutes to move, thereby improving the conductivity[22]. Heo *et al.* prepared poly(2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt-*co*-acrylamide)/sodium caseinate hydrogel (P(AMPSs-co-AAm)/SC hydrogel)[23]. On account of the existence of an ionized sulfone group and sodium ions, the AMPS chains uniformly combined into the hydrogel network serve as ion transport carriers to achieve conductivity [Figure 1A][23]. Zhou *et al.* synthesized a poly(acrylicacid-co-1-vinyl-3-butyl imidazole bromide) hydrogel (AAV hydrogel) [Figure 1B]. The aluminum ion and ion source provided by 1-vinyl-3-butylimidazolium bromide (VBIMBr) increased the electrolyte hydrogel's current-carrying concentration, so that the conductivity of the AAV hydrogel was greatly improved[24]. As a result of the excellent hydration of ions in polymer chains, hydrogels show high swelling in water. However, with the shielding effect of external ions on the interaction between polyelectrolyte and water, these hydrogels will shrink greatly in salt solutions, while the decrease of contact area with the salt solution will reduce the conductivity of hydrogels. Simultaneously, the strong interaction between mobile ions and cation/anion hydrogels will affect the conductivity of ions and zwitterionic polyelectrolytes are more conducive to ion transport[11].

Zwitterionic polymers have been introduced into hydrogels to achieve better conductivity. Cations and anions of zwitterionic polymers are covalently linked to the polymer backbone[25]. As zwitterionic ions migrate, their cations and anions play the role of counterions that are easy to separate, resulting in high ionic conductivity[26]. The conductivity of electrolyte materials produced by zwitterionic ions is seven times higher than pure polyelectrolytes. Peng *et al.* developed a poly(propylsulfonate dimethylammonium propylmethacrylamide)/lithium chloride (PPDP/LiCl) electrolyte hydrogel [Figure 1C], which exhibited electrostatic interactions between the charged groups and water molecules[27]. When an external electric field is applied, a hydration layer (natural ion migration channel) is formed along the polyzwitterion chain between the two electrodes, thereby significantly improving ion transport. Simultaneously, cation Li^+ and anion Cl^- are separated in the ion migration process to form polymer conductivity[27]. Diao *et al.* prepared polyvinyl alcohol/poly (covalent/noncovalent hybrid crosslinked acrylamide and sulfobetaine methacrylate copolymer) DN gels [Figure 1D][28]. Due to the counterion action in highly charged zwitterionic SBMA (NH^+ is positively charged and SO_3^- is negatively charged), the gel also exhibits excellent ionic conductivity[28].

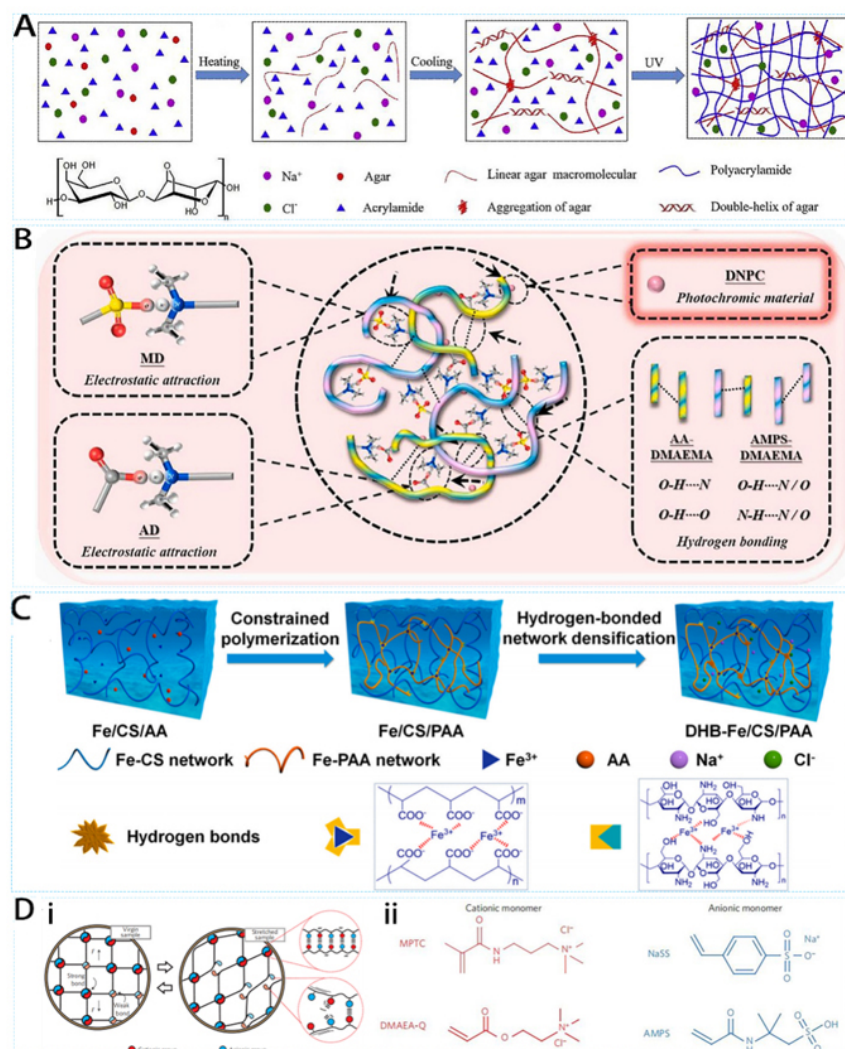## NETWORK TYPES OF POLYELECTROLYTE-BASED CONDUCTIVE HYDROGELS

Polyelectrolyte-based conductive hydrogels have been widely used in flexible sensors, electronic devices, and other fields, because of their good water retention capacity and excellent electrochemical properties[29,30]. However, the application of polymer conductive hydrogels in devices demands them to have good toughness, self-healing performance, tensile strength, and so on. The superior internal structure comes from the unique preparation method. Some common network types of polyelectrolyte-based conductive hydrogels are summarized below.

Double networks

Breakage of hydrogels is often attributed to the low density of polymer chains and the small friction between them. When an external force acts on heterogeneous hydrogel, the stress is mainly applied upon the shortest chain, which makes the polymer chain break, thus forming cracks on the hydrogel and finally leading to fracture. The results reflect that the fracture toughness of hydrogel can be enhanced by adding a neutral polymer network with relatively high molecular weight to the heterogeneous polyelectrolyte network[31]. Diao *et al.* used reversible non-covalent interacting crosslinked polyvinyl alcohol as one network and covalent/non-covalent hybrid crosslinked acrylamide, sulfobetaine methacrylate copolymer [P(AM-co-SBMA)] as the second network[28]. During deformation, reversible hydrogen bonds and electrostatic interactions in the double network dissipate energy as sacrificial bonds, and broken bonds can be reformed during recovery, thus endowing hydrogel with excellent tensile properties and self-healing ability[28]; The double-network hydrogel was made with agar, sodium chloride, and polyacrylamide by Hou *et al.* [Figure 2A][32]. Its fracture stress is 400 kPa and its strain is 1920%, demonstrating excellent tensile properties[32].

Ionic-hydrogen bond networks

Hydrogen and ionic bonds determine the properties of a large part of polyelectrolyte-based hydrogels. Strong ionic bonds can construct the skeleton structure of hydrogels, while sub-strong ionic bonds can endow them with better flexibility. On account of the reversibility of ionic bonds and the electrostatic interaction, polyelectrolyte hydrogels have strong toughness, good electrical conductivity, and fast self-healing ability. A composite electrolyte with binary polymer ionic liquid as the skeleton and an ionic liquid filled between skeleton segments has high-speed self-healing ability, high strength flexibility, and good ionic conductivity, as confirmed by Tian *et al.*[33]. Compared with covalent bonds and ionic bonds, hydrogen bonds are weaker, but the mechanical properties of hydrogels can be enhanced by cooperating with them. Because of the reversibility of hydrogen bonds, the self-healing ability of hydrogels is greatly improved.

Figure 2. Preparation of different types of polyelectrolyte-based conductive hydrogels. (A) Schematic diagram of the preparation of agar/NaCl/polymerizing polyacrylamide (PAM) ionic DN hydrogels[32]. (B) Schematic and mechanism of preparing final hydrogels (polymerizing AA-DMAEMA monomers/polymerizing AMPS-DMAEMA monomers/2,2-diphenyl-2H-naphtho [1,2-b] pyran-6-carbaldehyde) (PAD/PMD/DNPC) by free-radical polymerization of AMPS, AA and DMAEMA in deionized water at room temperature[35]. (C) Schematic illustration of preparation procedures of densified hydrogen-bonded Fe/CTS/PAA hydrogel (DHB-Fe/CTS/PAA) through hydrogel network constrained polymerization and hydrogen-bonded network densification processes[36]. (D) Schematic of physical hydrogels composed of polyampholytes. (i) Illustration of polyampholyte networks with ionic bonds of different strengths. The strong bonds serve as permanent crosslinking points and the weak bonds act as reversible sacrificial bonds that rupture under deformation. (ii) Chemical structures of monomers used in this work. Cationic monomers: 3-(methacryloylamino) propyl-trimethylammonium chloride (MPTC), N-dimethylamino ethylacrylate (DMAEA-Q); anionic monomers: sodium p-styrenesulphonate (NaSS), AMPS[39]. (A) Reproduced with permission[32]. Copyright 2019, Elsevier. (B) Reproduced with permission[35]. Copyright 2022, Elsevier. (C) Reproduced with permission[36]. Copyright 2021, Elsevier. (D) Reproduced with permission[39]. Copyright 2013, Springer.

Xu *et al.* designed a polyurethane connected by weak hydrogen bonds to ensure the material's toughness and good self-healing ability[34]. Therefore, Ye *et al.* prepared a new polyelectrolyte hydrogel with three graded ionic-hydrogen bond networks[35]. The structure of the hydrogel was designed using strong ionic bonds between units of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and 2-(dimethylamino)-ethyl methacrylate (DMAEMA), medium ionic bonds between units of acrylic acid (AA) and DMAEMA and weak hydrogen bonds between units of AMPS, AA and DMAEMA [Figure 2B]. The adhesion strength of hydrogels is more than 10.00 MPa and their self-healing ability is more than 90%

within 30 min, thereby showing a good self-adhesion and self-healing force[35].

Hydrogen bond networks

A dense hydrogen bond network structure is crucial for improving the tensile properties and deformation resistance of hydrogels. Song *et al.* formed a hydrogel structure with an anionic Fe^{3+}-coordinated polyacrylic acid network (Fe-PAA) and cationic Fe^{3+}-coordinated chitosan network (Fe-CTS) [Figure 2C][36]. They activated Fe-PAA and Fe-CTS networks by creating a salt impregnation environment, thus forming a dense hydrogen bond network between them[36]. In the process of hydrogen bond network densification [Figure 2C], due to the electrostatic interaction, AA is polymerized in the limited space of the polyelectrolyte network skeleton of the cationic Fe-CTS network, which ensures the molecular recombination of the anionic Fe-PAA and cationic Fe-CTS networks. Simultaneously, it also effectively prevents any possible flocculation. After that, the introduction of a high concentration salt partly destroys the ionic complexation between Fe-PAA and Fe-CTS hydrogel networks, leading to an intensive hydrogen bond interaction between the two networks and uniform complexation.

Physically crosslinked networks

A physically crosslinked network is often one of the layers of a double network. Unlike the chemically crosslinked first network, which relies on sacrificing bonds to achieve a gel toughness enhancement, the physically crosslinked first network toughens hydrogels through different mechanical enhancement mechanisms, such as agar networks. An agar chain can provide a reversible and flexible structure and its continuous breakage is controlled by the chain pull-out mode[37], thus dissipating the energy in the network and achieving a toughness enhancement. A large number of studies have also found that introducing a polysaccharide gel into an irreversible covalent network as a reversible physical network can greatly increase the number of single networks. Chen *et al.* proved that its toughness is related to its concentration[38]. Through the design of an agar gel network and a test of different gel concentrations higher than critical values, the stiffness and toughness of physical crosslinking could be enhanced, achieving an average stiffness of 313 kPa and a high toughness of 1089 J/m². Sun *et al.* designed the physical crosslinking network of a polyamide polymer hydrogel [Figure 2D][39]. In polymers, the anions and cations in polymers are distributed at random, which also makes a difference in the strength of the ionic bonds inside the hydrogel. Strong ionic bonds, as a skeleton, can permanently crosslink and will not be easily destroyed, which is the basic structure of hydrogel elasticity. Because of the reversibility of weak ionic bonds, they can be reformed after breaking and consuming energy. In addition, reversibility can be used to enhance their self-healing ability through bonding fractures and forming sacrificial networks. Through the combination of ionic bonds with different strengths, various mechanical properties of physical hydrogels in a certain range can be coordinated[39].

Different network structures can give different properties to polyelectrolyte conductive hydrogels. The relationship between properties and structure is summarized in Figure 3.

PROPERTIES OF POLYELECTROLYTE-BASED CONDUCTIVE HYDROGELS

To better promote the application of polyelectrolyte-based conductive hydrogels, simple conductivity cannot meet the demand and various properties, such as stretchability, flexibility, and adhesion, are required to aid its popularization and application. For example, flexible sensors used for human motion detection must tightly adhere to the skin. Simultaneously, hydrogels must have good mechanical properties and sufficient self-healing ability to cope with the damage from human motion, so as to realize the long-term use of hydrogels. Some common properties of polyelectrolyte-based conductive hydrogels are summarized below.
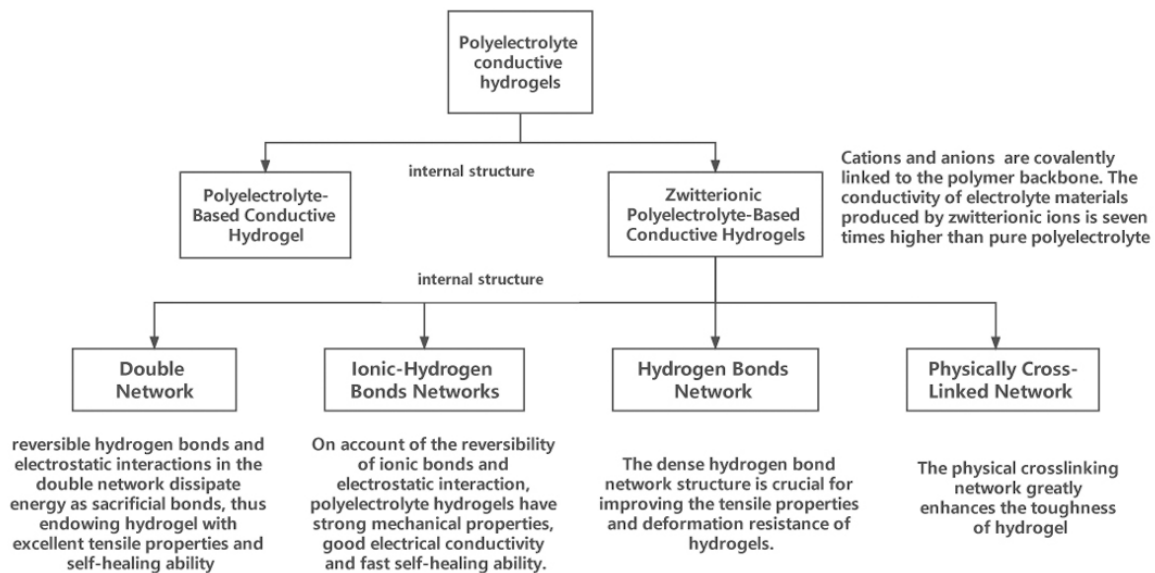
Figure 3. Different network structures resulting in different properties for polyelectrolyte conductive hydrogels.

Conductivity

Conductivity, as one of the basic indicators of sensor performance, affects the overall sensitivity and power consumption of the sensor to a certain extent. The conductivity of polyelectrolyte hydrogels mainly comes from the movement of ions inside the gel. Therefore, the optimization of conductivity can be carried out from two aspects, namely, the ion concentration and the three-dimensional structure that facilitates ion movement. The semi-dissolution acidification sol-gel transition (SD-A-SGT) has been proved as an effective method to improve the properties of hydrogels for both these aspects.

Using the anti-polyelectrolyte effect, Peng *et al.* prepared a conductive physical chitosan/sodium alginate conductive hydrogel by adding inorganic electrolyte salts in small molecular weight into the SD-A-SGT [Figure 4A][40]. This transformed the antagonistic effect between inorganic salt ions and the polyelectrolyte hydrogel into a synergistic effect, significantly increased the inorganic salt content, increased the inorganic salt mobility, and then increased the conductivity up to 2.96×10^{-1} S·cm^{-1} [Figure 4B]. Zhao *et al.* prepared a polyelectrolyte composite hydrogel (PECH) of chitosan (CTS) and sodium alginate (SA) by the SD-A-SGT[41]. The PECH exhibits a conductivity of 0.051 S·cm^{-1}. The CTS-SA PECH mainly forms a three-dimensional crosslinking network through the strong electrostatic interaction between CTS and SA, which provides a channel for electrolyte ion migration, contributing to its high conductivity[27]. Diao *et al.* prepared a kind of PVA/P (AM-co-SBMA) (polyvinyl alcohol/acrylamide and sulfobetaine methacrylate copolymer) containing many zwitterionic polyelectrolytes with a large number of charges[28]. Experiments show that the conductivity of PVA/PAM gel itself is very low. With an increase in the SBMA mass fraction to 15%, the conductivity of the PVA/P (AM-co-SBMA) gel reaches 7.49 S·m^{-1}[28].

Toughness

Skin sensors realize perception and response characteristics by following human skin behavior[42]. However, human behavior is irregular and various deformation behaviors occur, so strong toughness is an essential element. Polyelectrolyte hydrogels have become perfect materials for fabricating skin sensors on account of their excellent conductivity, biocompatibility and water retention, so it is necessary for hydrogels to have sufficient toughness to meet the needs of human motion. However, the toughness of polyelectrolyte hydrogels is often not satisfactory.
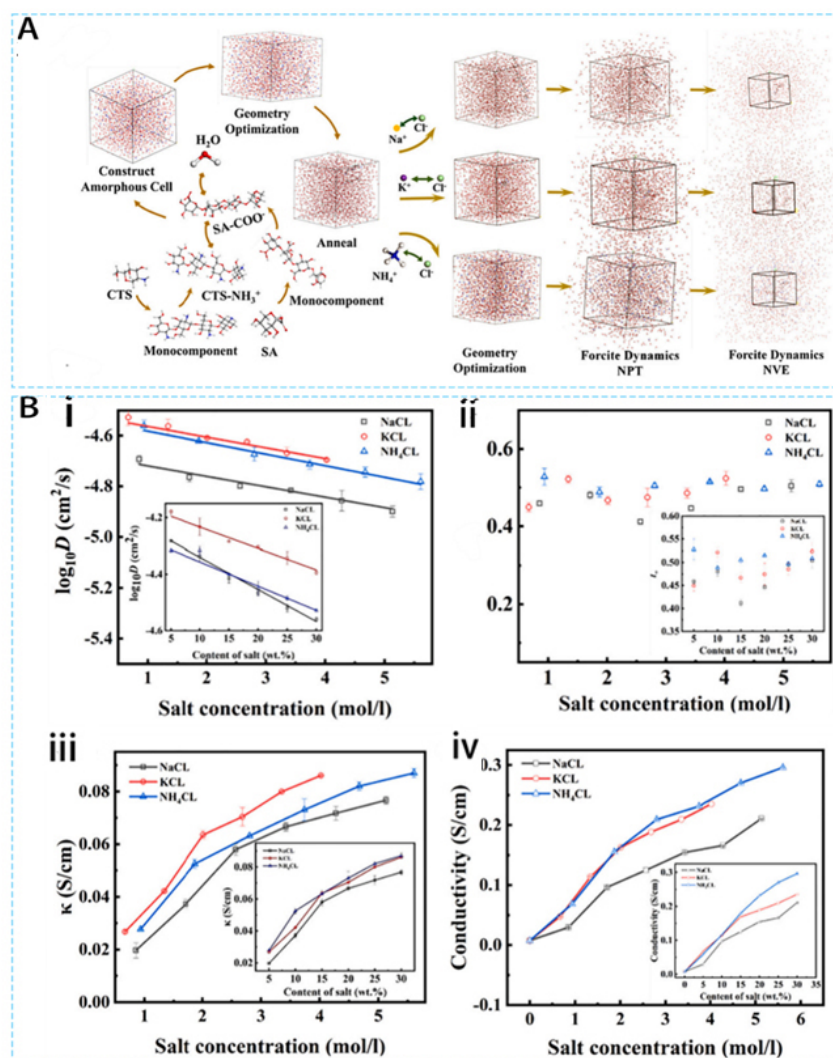
Figure 4. Molecular simulation process and results. (A) Schematic diagram of the molecular simulation process. (B) Molecular simulation results of CTS-SA CHs containing different inorganic salts for (i) diffusion coefficient; (ii) ion migration number; (iii) simulated ionic conductivity; and (iv) experimental ionic conductivity[40]. (A and B) Reproduced with permission[40]. Copyright 2022, Elsevier.

The existing methods to enhance the toughness of polyelectrolyte hydrogels are mainly divided into two types. One type is to add another hydrogel network according to the type of hydrogel matrix to construct a double-network hydrogel structure[43,44]. Double-network hydrogels composed of hard-brittle and soft-ductile networks have excellent mechanical properties[45]. Wei *et al*. prepared a polyacrylamide (PAA)-alginate hydrogel with perfect toughness[44]. They used microfluidic technology to prepare double-network hydrogels by controlling the flow rates of two liquid phases, namely, $CaSO_4$/tetramethylethylenediamine (TEMED) and PAA/alginate. The resultant hydrogel has excellent toughness and elasticity [Figure 5A]. The other one to increase toughness is to use other polyelectrolytes with equivalent opposite charges to form polyionic complexes with the original hydrogel matrix[46,47]. Huang *et al*. prepared a tough double-network polyelectrolyte complex hydrogel by infiltrating zwitterionic poly(sulfobetaine acrylamide) (PSBAA) into an expanded poly(lysine acrylamide) (PLysAA) network and polymerizing under ultraviolet irradiation[47]. The best properties were found to be 1073 kPa for stress, 459% for strain, and 507 kPa for Young's modulus[47].
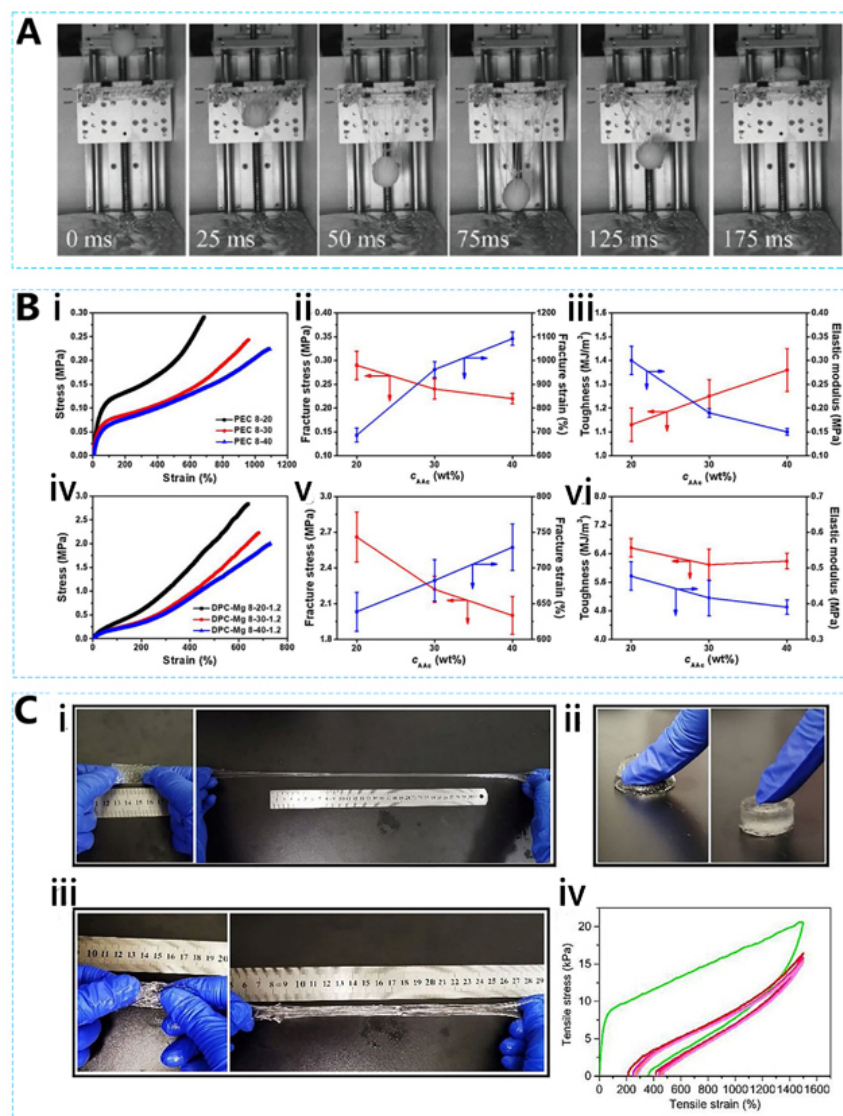
Figure 5. Demonstration of the toughness of hydrogels. (A) A series of optical images showing an egg of 60 g impacting onto a printed web from a height of 1 m and it remaining intact. (B) Tensile stress-strain curves, with the corresponding (ii and v) fracture stress and strain and (iii and vi) toughness and elastic modulus of the PEC and DPC-Mg hydrogels prepared with various cAAc[49]. (C) CTS/P(AA-HEMA) organogels with extraordinary mechanical properties. (i) Original organogel and after stretching over 10,000%. (ii) An organogel compressed and immediately recovered to its original state after releasing the stress. (iii) Two organogels tied together and stretched. (iv) Loading-unloading experiments of CTS/P(AA-HEMA) organogels during five successive loading-unloading cycles at a set strain of 1500%[50]. (A) Reproduced with permission[44]. Copyright 2018, ACS. (B) Reproduced with permission[49]. Copyright 2020, Elsevier. (C) Reproduced with permission[50]. Copyright 2020, Elsevier.

Salt in high concentrations is one of the necessary conditions for the excellent conductivity of polyelectrolyte-based conductive hydrogels. Simultaneously, however, high concentrations of salts also destroy physical bonds, such as hydrogen bonds. As a result of the salting-out effect, the toughness is degraded. A Fe/CTS/PAA hydrogel with a dense hydrogen bond network was prepared by Song *et al.*[36]. In the deformation process, the dense hydrogen bond interaction consumes energy whilst breaking[48], which gives excellent toughness to Fe/CTS/PAA. Cao *et al.* prepared an ionic crosslinked CTS/PAA hydrogel with double physical crosslinking (DPC)[49]. There is a strong electrostatic interaction between the concentrated CTS, polyacrylic acid (PAAc), polymer chain, and cation/anion, which can function as a "sacrificial bond"

to consume energy, so that the hydrogel does not break when distorted [Figure 5B][49]. Han *et al.* prepared a chitosan/poly(hydroxyethyl acrylate-acrylate) (CTS/P(AA-HEMA)) organic gel based on the hydrogen bond interaction[50]. These hydrogen bond interactions endowed the CTS/P(AA-HEMA) organic gel with extraordinary mechanical properties, including a tensile strain of more than 12,000% [Figure 5C][50]. The physical crosslinking hydrogen bond interaction effectively dispersed the stress applied to the DN organic gel[51].

To compare the conductivity and toughness of different polyelectrolyte-based conductive hydrogels, the components of the polymer networks and the conductivity, tensile stress and tensile strain of some polyelectrolyte-based conductive hydrogels are summarized in Table 1.

Self-healing properties

The self-healing property of a hydrogel is the ability to repair its own structure and restore its mechanical properties after being damaged by an external force. The self-healing property of the hydrogel can enhance its own durability. Constitutional dynamic chemistry (CDC) is the theoretical support for the preparation of various kinds of self-healing hydrogels. "Dynamic" is one of the features of CDC. Dynamic polymer networks can be prepared by dynamic bonding. Dynamic polymer networks are capable of dynamic/reversible bond breaking-reformation reactions, so they have the ability to self-repair. In other words, the structure of a self-healing gel can be restored to its original state and further restore its original properties after being destroyed [Figure 6A]. The self-healing mechanisms of hydrogels include physical and chemical self-healing[52]. Physical self-healing hydrogel depends on non-covalent interactions, such as hydrogen bonds and electrostatic interactions. For chemical-healing, covalent interactions including boron-oxygen (phenylboronate ester) and sulfur-sulfur (disulfide) bonds are important.

To increase the self-healing properties of hydrogels, we need to choose proper materials to build non-covalent and covalent interactions, which are related to the physical and chemical self-healing mechanism. Yuan *et al.* prepared a polydiallyldimethyl ammonium chloride (PDDA)/branched polyethyleneimine (PEI)-polysodium 4-styrene sulfonate (PSS)/polyacrylic acid (PAAc) (PDDA/PEI)-(PSS/PAAc) polyelectrolyte conductive hydrogel[53]. The hydrogen bonds and electrostatic interactions between PAAc, PSS, PEI, and PDDA on the fracture surface of the (PDDA/PEI)-(PSS/PAAc) hydrogel can break and heal dynamically. Therefore, the polyelectrolyte on the broken surface can reconstruct hydrogen bonds and electrostatic interactions, thus finely healing the broken hydrogel [Figure 6B and C][53]. Fang *et al.* prepared a weak polyelectrolyte-based hydrogel with a self-healing property by polymerizing acrylic acid and poly(ethylene glycol) methacrylate[54]. After the gel was cut off, it was soaked in NaCl and the salt solution could break some electrostatic and hydrogen bond interactions on the cut surface and promote chain migration. When in contact, interactions between the electrostatic and hydrogen bonding can be reconstructed by chain diffusion on the damaged surface to heal the broken hydrogel. As shown in Figure 6D, the gel after healing can complete the tensile operation and can withstand a tensile force of 500 g[54]. Diao *et al.* tested the internal damage process of a PVA/P (AMCO-SBMA) DN gel under different strain forces of 100%-500%[28]. In addition, the softness parameter, i.e., the initial elastic modulus loss percentage ($1-E_x/E_0$), was proved by experiments and the toughness recovered to 65% and 77%, and the hardness recovered to 75% and 81%, respectively, after standing for 5 and 10 min under the loading of 300% strain force, which were attributed to the dynamic, crosslinkable and effective dissociation-association process[28].

Freezing resistance

In hydrogels, water acts as a conductive medium, but its evaporation and freezing are inevitable. When temperatures are extremely high or low, conductive hydrogels become hard and non-conductive, which

**Table 1. Common polyelectrolyte-based conductive hydrogels**

Type	Components of polymer networks	Conductivity	Tensile stress	Tensile strain	Ref.
Double network	PVA &P(AM-co-SBMA)	7.49 S·m^{-1}	--	970%	[28]
	Agar&Polyacrylamide	--	400 kPa	1920%	[32]
Ionic-hydrogen bonds networks	polyurethane connected by weak hydrogen bonds	--	1.56 ± 0.03 gPa	--	[34]
	Triple gradual ionic-hydrogen bonds network	0.672 S·m^{-1}	1 mPa	--	[35]
Hydrogen bonds network	DHB-Fe/CTS/PAA	--	~0.34 mPa	~1370%	[36]
Physically crosslinked network	Polyampholytes	--	2.6-0.07 mPa	940%-1000%	[39]
	polymers bearing randomly dispersed cationic and anionic repeat groups		--	1000%	

reduce their durability and stability in practice[55], which obviously hinders their application in real life[56]. Therefore, it is very important to prepare freeze-resistant polyelectrolyte conductive hydrogels to ensure normal operation under extreme conditions. Adding inorganic salts, organic compounds, or organic solvents to gels is an effective method to reduce the freezing point and improve the frost resistance of hydrogels[57]. Cheng *et al.* prepared an antifreeze hydrogel by polymerizing polyacrylamide (PAM)/SA/2,2,6,6-tetramethylethylpiperidine-1-oxyl radical (TEMPO)-oxidized cellulose nanofibers (TOCNs) in a dimethyl sulfoxide (DMSO)/aqueous solution and then soaking CaCl$_2$ solution[58]. MSO formed hydrogen bonds with the free water, which protected the free water from crystallization and enhanced the antifreeze performance of the hydrogel. Simultaneously, calcium chloride also effectively prevented the formation of ice[59]. Zhao *et al.* used sodium chloride as a conductive salt to prepare a conductive hydrogel by polymerizing acrylamide and N-(3-aminopropyl) in a glycerol-water binary solvent[60]. The hydrogel is still highly transparent even if it is stored at -80 °C for more than three months and its antifreeze mechanism is superior[60] by using the mechanism of strong hydrogen bond between glycerol and water molecules[61].

Stickiness

Adhesion is an important index when a hydrogel is applied to electronic sensing equipment[62]. A good hydrogel sensor needs to be closely attached to human skin through good adhesion in order to accurately detect human motion and obtain detailed motion indexes[63]. The stickiness of hydrogels mainly comes from interactions with the surfaces of other materials, including hydrogen bonding, hydrophobic interactions, metal complexation, and/or electrostatic effects[64]. Fu *et al.* designed a lignin-reinforced hydrogel[65]. Because lignin is rich in phenolic hydroxyl and other polar functional groups, it has strong adhesion, thus improving the adhesion of the hydrogel [Figure 7A-C][65]. Wang *et al.* used poly(ethylene glycol) dimethacrylate (PEGDMA) as a crosslinking agent and zwitterionic polyelectrolyte (ZPE) hydrogels were fabricated by copolymerization of [2-(methacryloxy) ethyl] dimethyl (3-sulfopropyl) ammonium hydroxide (SBMA) and AMPS (or [2-(acryloyloxy)ethyl]trimethylammonium chloride solution, DAC)[66]. The stickiness strength to skin was 1-4 kPa, on account of the interactions provided by the zwitterionic fraction, including the dipole-dipole interaction, electrostatic interaction and hydrogen bonding between the gel and skin surface [Figure 7D][66].

In addition to the above properties, polyelectrolyte hydrogels are closer to living tissues than other synthetic biomaterials because of their special hydrophilic and obvious swelling properties. After absorbing water, their friction and mechanical effects on surrounding tissues and cells are obviously reduced and they have good biocompatibility and cell compatibility[28,67,68]. Simultaneously, new materials can be added into the polyelectrolyte gel conductive hydrogels to endow them with new properties, including good antibacterial activity by adding nanoparticles and antibiotics with antibacterial properties[69,70]. The addition of natural
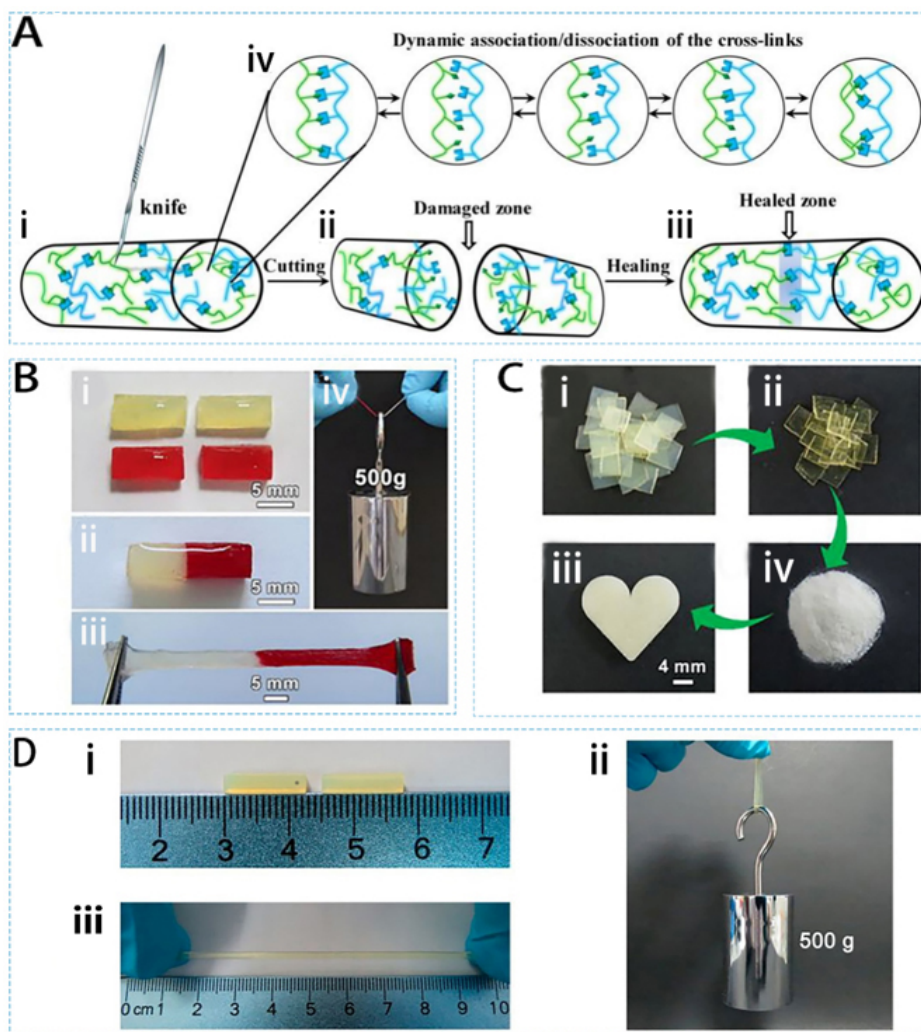
Figure 6. Schematic diagram and mechanism of self-healing properties of hydrogels. (A) Schematic illustration of self-healing mechanisms of self-healing gels based on CDC. (i) A cylindrical self-healing gel is cut by a knife. (ii) The gel is cut into two pieces and the functional groups stay dissociated across the damaged zone. (iii) The crack is healed by the reformed dynamic bonds after the fractured surface contacting each other. (iv) The dynamic association and dissociation of the reversible crosslinks based on CDC[52]. (B) Digital photographs of undyed and dyed (16% PDDA/PEI)-(20% PSS/PAAc) hydrogel cuboids that were cut into two pieces (i) and the separated pieces with different colors were well healed at room temperature for 14 h (ii). The healed hydrogel with a width of 4 mm and a thickness of 1.1 mm can be stretched to a length 6.6 times longer than its original length without fracture (iii) and hold a weight of 500 g (iv)[53]. (C) Digital photographs of (16%PDDA/PEI)-(20%PSS/PAA) hydrogel sheets that were cut into small pieces (i) and then dried in a vacuum oven at room temperature for 24 h (ii). The dried hydrogel pieces were ground into powders (iii) and then reshaped into a heart-shaped hydrogel (iv)[53]. (D) Use of acrylic acid and poly(ethylene glycol) methacrylate to fabricate polyelectrolyte-based hydrogels with excellent self-recovery. (i) The hydrogel is cut into two parts. (ii and iii) The healed sample can withstand stretching and lift a weight of 500 g[54]. (A) Reproduced with permission[52]. Copyright 2014, RSC. (B and C) Reproduced with permission[53]. Copyright 2019, ACS. (D) Reproduced with permission[54]. Copyright 2019, ACS.

polymer materials, such as chitosan and gelatin, can endow polyelectrolyte hydrogels with good biodegradability and promote their application in the fields of tissue engineering and biomedical materials[68,71].

APPLICATIONS OF POLYELECTROLYTE-BASED CONDUCTIVE HYDROGELS
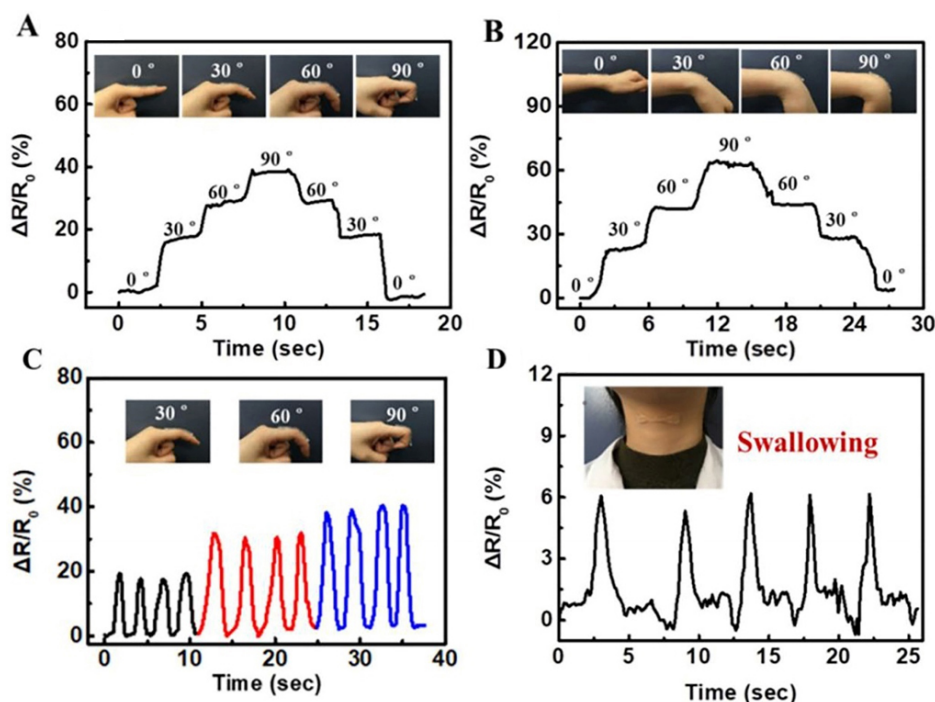### Strain sensors
In recent years, the demand for wearable electronic devices has been increasing exponentially[72], especially
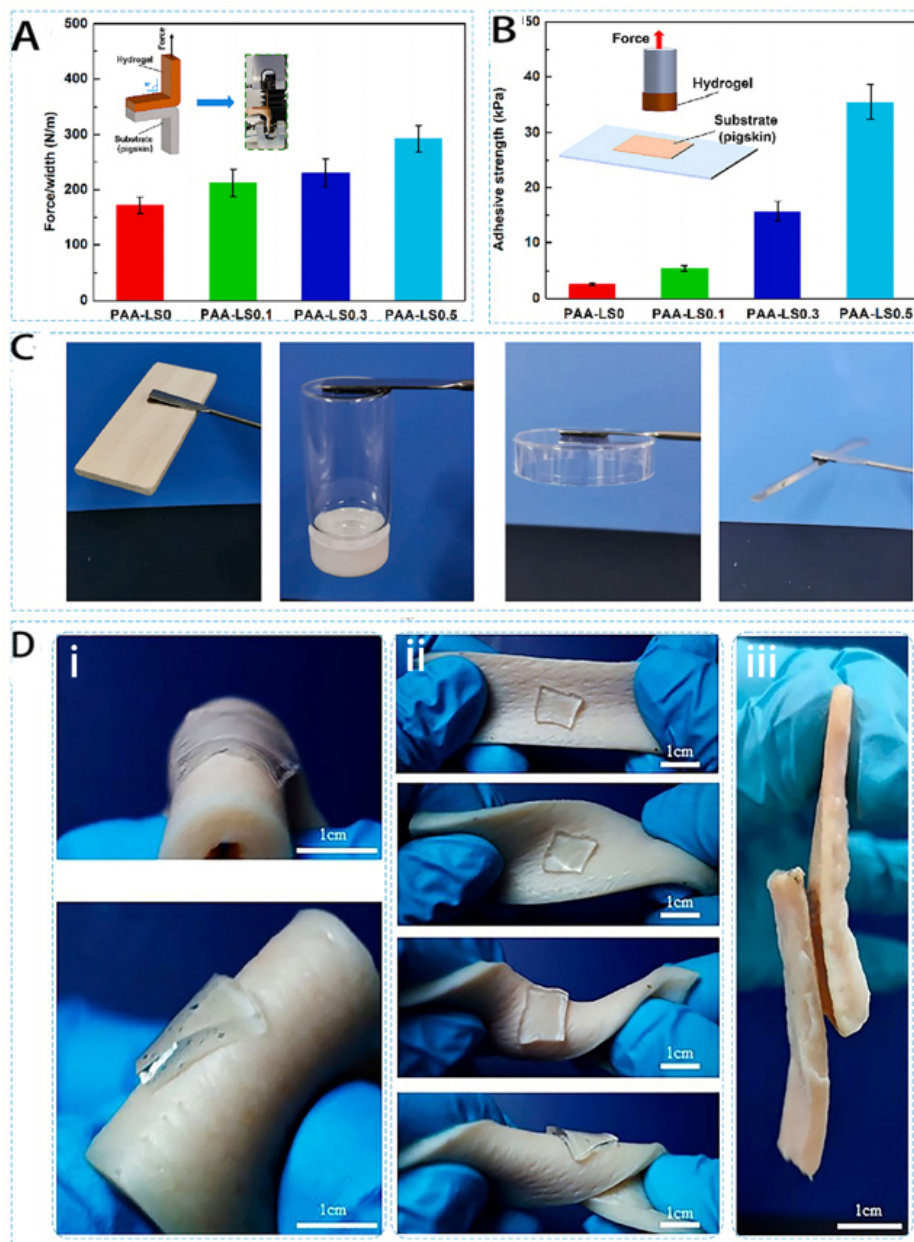
Figure 7. Adhesion tests of hydrogels. (A) Peeling tests of hydrogels [various lignosulfonate (LS) contents] adhering to pigskin[65]. (B) Adhesion strength of hydrogels (various LS contents) adhering to pigskin[65]. (C) Schematic diagram of hydrogel adhesion to wood, glass, plastic, and stainless steel spoons[65]. (D) Adhesion of the hydrogel to pig skin. Hydrogels adhered to pig skin tissues under bending (i) and torsion (ii). (iii) Two pig skins connected by hydrogel[66]. (A-C) Reproduced with permission[65]. Copyright 2022, Elsevier. (D) Reproduced with permission[66]. Copyright 2020, ACS.

in human motion detection and health monitoring. The principle is that mechanical signals can be converted into electrical signals according to the changes of parameters, such as the resistance and capacitance of hydrogels during mechanical deformation[73]; thus, human body indicators can be detected according to the changes of electrical signals. Zhang *et al.* designed a highly transparent injectable chitosan/polyzwitterionic double-network hydrogel with self-healing and self-adhesive abilities[74]. Citrate ions act as charge carriers and migrate in the polymer through the movement of polyelectrolyte chains to realize the conductivity of the hydrogel. However, when the gel is deformed, this effect is not strong and

Figure 8. Schematic diagram of the application of hydrogel strain sensor in detecting human motion. (A and C) Relative resistance changes of poly(sulfobetaine-co-acrylic acid)/chitosan-citrate (P(SBMA-co-AA)/CTS-Cit) DN hydrogel strain sensors at different angles of finger bending and (B) wrist bending. (D) Relative resistance changes of the hydrogel strain sensors when swallowing[74]. Reproduced with permission[74]. Copyright 2020, Elsevier.

unstable. On the contrary, in the deformation process, some of the original conductive paths become discontinuous or broken, which leads to great changes in resistance. As shown in Figure 8A-C, the hydrogel will deform with the bending of knuckles or wrists, leading to changes in the relative resistance, but it will have very stable resistance at a fixed angle. Apart from detecting large joint movements, hydrogel sensors are also highly sensitive and can detect subtle throat movements during swallowing activities [Figure 8D][74]. Sui *et al.* prepared ionic conductive hydrogel (lithium chloride polysulfobetaine methacrylate-acrylic acid hydrogel) with long-term antifreeze, water retention, and self-regeneration ability[75]. In the process of repeated stretching, it shows reversible resistance change, showing significant potential as a flexible resistance sensor. Simultaneously, the hydrogel solves the problems of water loss and poor conductivity caused by freezing at abnormal temperatures and broadens the application range of hydrogels as flexible sensors[75].

Solid-state supercapacitors
Solid-state supercapacitors can benefit from polyelectrolyte conductive hydrogels due to their ability to retain water and permit ion migration to improve the working stability of the capacitors. A PPDP hydrogel designed by Peng *et al.* provided water retention capacity for a gel electrolyte in the solid state by aggregating water molecules around charged groups[27]. Furthermore, the network structure of hydrogels can be used as ion transport channels, resulting in better electrochemical performance. PPDP was applied to graphene-based solid-state supercapacitors, and its performance reached 300.8 F·cm^{-3} at 0.8 A·cm^{-3} [Figure 9A-C][27].

Visual displays
Organic photochromic hydrogels can dynamically respond to changes in ultraviolet light intensity and
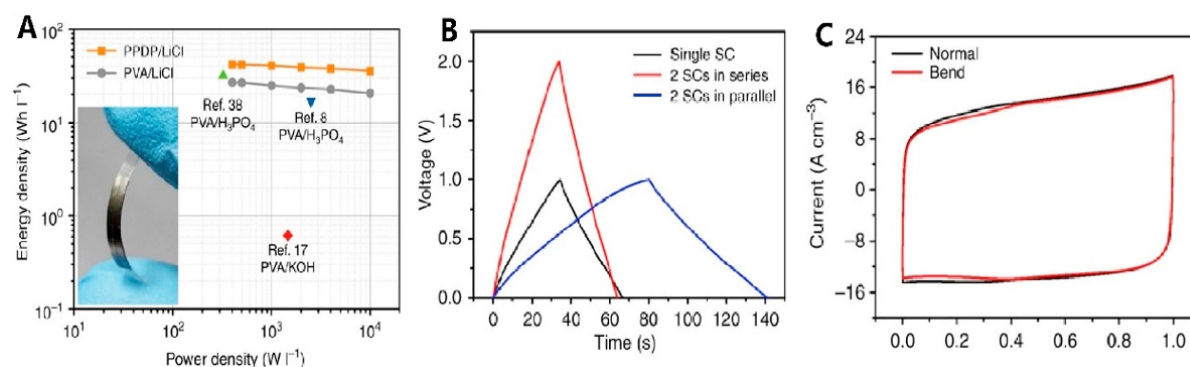
Figure 9. Effect diagram of PPDP applied to a graphene-based solid-state supercapacitor. (A) A typical Ragone plot of as-fabricated graphene-based solid-state supercapacitors. Inset is a prototype of graphene-based solid-state supercapacitor applying PPDP gel electrolyte with a planar configuration. (B) Galvanostatic charge-discharge curves of a single supercapacitor (SC) and two SCs connected in series and in parallel at 8 A·cm^{-3}. (C) Comparison of CV curves between normal and bent status (90°) and the scan rate is 50 mV·s^{-1} [27]. Reproduced with permission [27]. Copyright 2016, Springer.

reversibly change their color. Therefore, it can be widely used in visual displays. However, these hydrogels cannot be further applied because of their poor mechanical properties and service life. Because polyelectrolyte conductive hydrogels can be endowed with self-healing ability and stretchability by changing the network structure, people began to consider preparing polyelectrolyte conductive hydrogels into organic photochromic hydrogels, so as to solve some shortcomings of organic photochromic hydrogels and promote their better popularization and application. A kind of multifunctional polyelectrolyte hydrogel with gradual ionic-hydrogen bonds network prepared by Ye *et al.*[35]. In addition to giving it excellent photochromic properties [Figure 10], it also gives it good mechanical properties, electrical conduction, self-repairing ability, adhesion, and pH sensitivity, which fundamentally solves the defects of photochromic hydrogel in mechanical properties and service life, thus increasing its practical application value[35].

Wound dressing

The conductivity of polyelectrolyte-based hydrogels comes from their anions and cations and different ions endow hydrogels with different properties, so polyelectrolyte-based conductive hydrogels will have strong adjustability and can be applied to different fields other than conductive materials. At present, many researchers have regarded polyelectrolyte-based hydrogels as good choices for wet wound dressings. The reason is that hydrogels can simulate a moist environment for wound healing similar to the physiological state, promoting skin cell division and speeding up the healing process. However, it is difficult to make hydrogels that have high antibacterial activity and excellent biological safety at the same time[76,77]. At present, a popular breakthrough in this problem is to prepare physical hydrogels from natural anionic and cationic polyelectrolytes. These gels have excellent biocompatibility and biodegradability. They can carry nanoparticles with antibacterial properties, which makes them gradually become the first choice for preparing wound dressing substrates[70,78]. Chitosan/carboxymethyl chitosan/silver nanoparticles (CTS/CMCTS /AgNPs) polyelectrolyte hydrogel prepared by Yang *et al.*, which is loaded with AgNPs, can ensure that the wound is not polluted by bacteria, adjust the arrangement of collagen and promote the skin structure to return to normal[79]. Simultaneously, natural polymers can enhance cell proliferation and extracellular matrix formation, thus reconstructing the barrier between tissue and the external environment and achieving the purpose of wound recovery [Figure 11][79].

Drug delivery

In the medical field, polyelectrolyte-based hydrogels can not only achieve antibacterial properties or other medical uses by loading nanoparticles with antibacterial properties but by changing their anion and cation
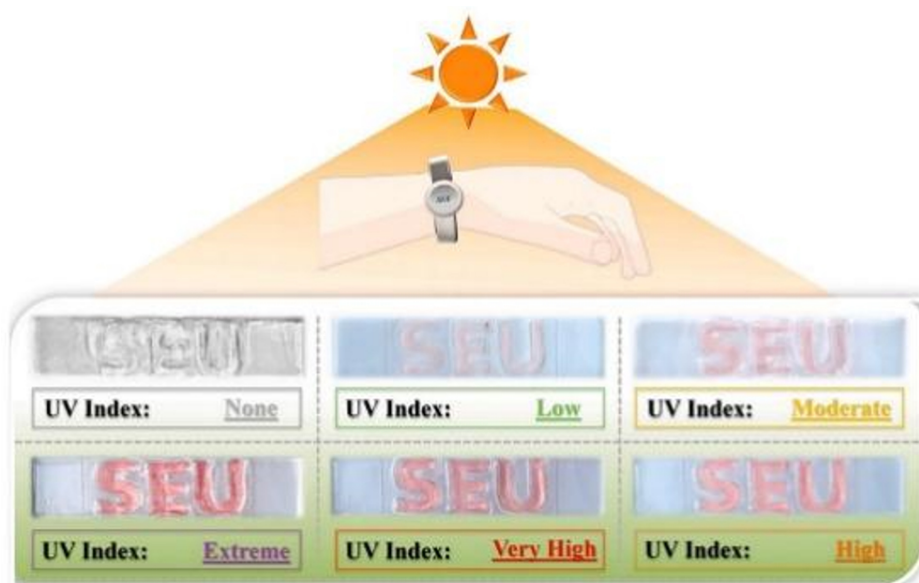
Figure 10. Polyelectrolyte-based hydrogel used for visual displays. Hydrogel with the pattern "SEU" have photochromic behavior under different direct ultraviolet intensities[35].Reproduced with permission[35].Copyright 2022, Elsevier.
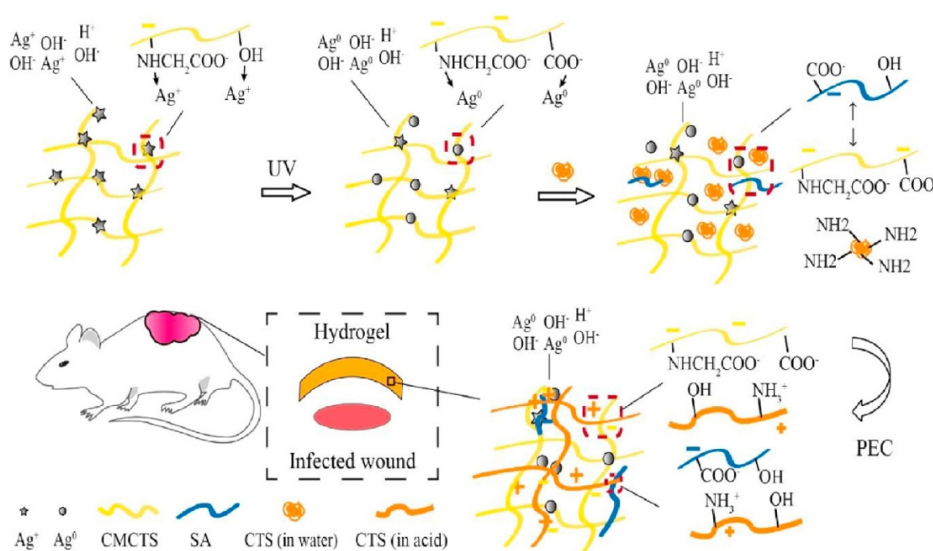
Figure 11. Schematic diagram of CTS/CMCTS/AgNPs hydrogel preparation and application process. The microcosmic illustration of hydrogel for in situ photoreduction and SD-A-SGT and its use in wound closure. Reproduced with permission[79].Copyright 2020, Elsevier[79].

raw materials can also make the hydrogels have some properties of their raw materials to achieve a better effect. For one example, chitosan is a positively charged polyelectrolyte in solution. Due to its good biocompatibility and skin adhesion, it has been gradually used in the preparation of hydrogels for drug delivery in the past two decades[80]. Hu *et al*. prepared salecan/chitosan PEC hydrogel loaded with vitamin C (VC), which can control the release by sensing the pH of the release medium[68]. In simulated gastric fluid (SGF), the carboxyl group of PEC hydrogels has strong hydrogen bond interaction due to protonation. These hydrogen bonds make the polyelectrolyte complex (PEC) network denser and can be used to prevent VC release. In contrast, when in simulated intestinal fluid (SIF), there is an obvious increase

in the release rate, and then it reaches the maximum value of 92.3% after 10 h. It has proved that this PEC hydrogel can overcome the stimulation of gastrointestinal irritation, realize the fixed-point release of VC, and can be used as a carrier for nutrient delivery[68].

In addition, polyelectrolyte conductive hydrogels also have a very broad application prospect in the fields of biological tissue engineering materials and touch panels. Nowadays, polyelectrolyte conductive hydrogels have become a research hotspot.

SUMMARY AND PERSPECTIVES

Because of their highly designable properties, hydrogels can have excellent electrical conductivity, mechanical properties, self-healing ability, freezing resistance, and adhesion by using appropriate raw materials and crosslinking methods, so they are potential candidates for new flexible electronics equipment. In this review, the development process of ionic and crosslinking methods for preparing various polyelectrolyte conductive hydrogels in recent years, and various properties and principles of conductive hydrogels are presented. Generally, conductive materials can be used in hydrogels as conductive fillers, as well as raw materials for building conductive frames. The introduction of inorganic salts and the formation of hydrogen bonds can provide hydrogels with certain self-healing and freezing resistance, and the existence of zwitterions can provide strong dipole interaction and electrostatic interaction, so that hydrogels can combine with skin surface by hydrogen bonds and make them have adhesion properties. At present, flexible strain sensors with different sensing modes have been gradually developed, which will provide a new choice for soft robots and medical health detection.

In the future, with the continuous popularization and application of flexible electronics materials and hydrogel dressings, new breakthroughs will be made in the field of polyelectrolyte-based conductive hydrogels. However, due to the widespread defect of water loss, hydrogels have not been widely produced and applied. For example, although hydrogels with certain freezing resistance have been developed recently, it is difficult to carry out large-scale and low-cost industrial production because of its complex manufacturing process and flow. In addition, current electronic devices are more focused on intelligence and integration. How to adjust various stimulation response performances of hydrogels according to the current situation will be a major problem in preparing hydrogel integrated intelligent electronic devices. Finally, a polyelectrolyte-based conductive hydrogel with excellent biodegradability, antibacterial activity, and biocompatibility has not been fully developed and applied. Generally speaking, we believe that there is a great potential for polyelectrolyte-based conductive hydrogels in many different application fields, and their development can also have a significant impact on human life and social production.

DECLARATIONS

Authors' contributions
Designed and wrote the original draft: Fan X, Chen Z, Sun H, Zeng S, Tian Y
Reviewed the manuscript: Liu R
Reviewed and revised the manuscript: Tian Y

Availability of data and materials
Not applicable.

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REFERENCES

1. Guiseppi-Elie A. Electroconductive hydrogels: synthesis, characterization and biomedical applications. *Biomaterials* 2010;31:2701-16. DOI PubMed
2. Li G, Li C, Li G, et al. Development of conductive hydrogels for fabricating flexible strain sensors. *Small* 2022;18:e2101518. DOI PubMed
3. Hu S, Zhou L, Tu L, et al. Elastomeric conductive hybrid hydrogels with continuous conductive networks. *J Mater Chem B* 2019;7 :2389-97. DOI PubMed
4. Gan D, Han L, Wang M, et al. Conductive and tough hydrogels based on biopolymer molecular templates for controlling in situ formation of polypyrrole nanorods. *ACS Appl Mater Interfaces* 2018;10:36218-28. DOI PubMed
5. Rong Q, Lei W, Liu M. Conductive hydrogels as smart materials for flexible electronic devices. *Chemistry* 2018;24:16930-43. DOI PubMed
6. Wang Z, Cong Y, Fu J. Stretchable and tough conductive hydrogels for flexible pressure and strain sensors. *J Mater Chem B* 2020;8:3437-59. DOI PubMed
7. Sun X, Yao F, Li J. Nanocomposite hydrogel-based strain and pressure sensors: a review. *J Mater Chem A* 2020;8:18605-23. DOI
8. Zhang YZ, El-Demellawi JK, Jiang Q, G et al. MXene hydrogels: fundamentals and applications. *Chem Soc Rev* 2020;49:7229-51. DOI PubMed
9. Wang Q, Pan X, Wang X, et al. Fabrication strategies and application fields of novel 2D Ti3C2Tx (MXene) composite hydrogels: A mini-review. *Ceram Int* 2021;47:4398-403. DOI
10. Vieira S, da Silva Morais A, Garet E, et al. Methacrylated gellan gum/poly-l-lysine polyelectrolyte complex beads for cell-based therapies. *ACS Biomater Sci Eng* 2021;7:4898-913. DOI PubMed
11. Lee CJ, Wu H, Hu Y, et al. Ionic conductivity of polyelectrolyte hydrogels. *ACS Appl Mater Interfaces* 2018;10:5845-52. DOI PubMed
12. Wei J, Zhou J, Su S, Jiang J, Feng J, Wang Q. Water-deactivated polyelectrolyte hydrogel electrolytes for flexible high-voltage supercapacitors. *ChemSusChem* 2018;11:3410-5. DOI PubMed
13. Rosso F, Barbarisi A, Barbarisi M, et al. New polyelectrolyte hydrogels for biomedical applications. *Mater Sci Eng C* 2003;23:371-6. DOI
14. Rao KM, Kumar A, Han SS. Polysaccharide-based magnetically responsive polyelectrolyte hydrogels for tissue engineering applications. *J Mater Sci Technol* 2018;34:1371-7. DOI
15. Lam J, Clark EC, Fong EL, et al. Evaluation of cell-laden polyelectrolyte hydrogels incorporating poly(L-Lysine) for applications in cartilage tissue engineering. *Biomaterials* 2016;83:332-46. DOI
16. Kwon HJ, Yasuda K, Gong JP, Ohmiya Y. Polyelectrolyte hydrogels for replacement and regeneration of biological tissues. *Macromol Res* 2014;22:227-35. DOI
17. Patil J, Kamalapur M, Marapur S, Kadam D. Ionotropic gelation and polyelectrolyte complexation: the novel techniques to design hydrogel particulate sustained, modulated drug delivery system: a review. *Dig J Nanomater Biostruct* 2010;5:241-8. DOI
18. Kwon HJ. Tissue engineering of muscles and cartilages using polyelectrolyte hydrogels. *Adv Mater Sci Eng* 2014;2014:1-7. DOI
19. Lu X, Yu M, Wang G, Tong Y, Li Y. Flexible solid-state supercapacitors: design, fabrication and applications. *Energy Environ Sci* 2014;7:2160-81. DOI
20. Zhu C, Yang P, Chao D, et al. All metal nitrides solid-state asymmetric supercapacitors. *Adv Mater* 2015;27:4566-71. DOI PubMed
21. Wu C, Lu X, Peng L, et al. Two-dimensional vanadyl phosphate ultrathin nanosheets for high energy density and flexible pseudocapacitors. *Nat Commun* 2013;4:2431. DOI PubMed
22. Yang C, Suo Z. Hydrogel ionotronics. *Nat Rev Mater* 2018;3:125-42. DOI

23. Heo S, Seo H, Song C, Shin S, Kwon K. Polyelectrolyte-derived adhesive, super-stretchable hydrogel for a stable, wireless wearable sensor. *J Mater Chem C* 2021;9:16778-87. DOI

24. Zhou Y, Fei X, Tian J, Xu L, Li Y. A ionic liquid enhanced conductive hydrogel for strain sensing applications. *J Colloid Interface Sci* 2022;606:192-203. DOI PubMed

25. Diao W, Wu L, Ma X, et al. Reversibly highly stretchable and self-healable zwitterion-containing polyelectrolyte hydrogel with high ionic conductivity for high-performance flexible and cold-resistant supercapacitor. *J Appl Polym Sci* 2020;137:48995. DOI

26. Tiyapiboonchaiya C, Pringle JM, Sun J, et al. The zwitterion effect in high-conductivity polyelectrolyte materials. *Nat Mater* 2003;3:29-32. DOI PubMed

27. Peng X, Liu H, Yin Q, et al. A zwitterionic gel electrolyte for efficient solid-state supercapacitors. *Nat Commun* 2016;7:11782. DOI PubMed PMC

28. Diao W, Wu L, Ma X, et al. Highly stretchable, ionic conductive and self-recoverable zwitterionic polyelectrolyte-based hydrogels by introducing multiple supramolecular sacrificial bonds in double network. *J Appl Polym Sci* 2019;136:47783. DOI

29. Wang D, Gong X, Heeger PS, Rininsland F, Bazan GC, Heeger AJ. Biosensors from conjugated polyelectrolyte complexes. *Proc Nat Acad Sci USA* 2002;99:49-53. DOI PubMed PMC

30. Cao B, Lee CJ, Zeng Z, et al. Electroactive poly(sulfobetaine-3,4-ethylenedioxythiophene) (PSBEDOT) with controllable antifouling and antimicrobial properties. *Chem Sci* 2016;7:1976-81. DOI PubMed PMC

31. Na YH. Double network hydrogels with extremely high toughness and their applications. *Korea-Aust Rheol J* 2013;25:185-96. DOI

32. Hou W, Sheng N, Zhang X, et al. Design of injectable agar/NaCl/polyacrylamide ionic hydrogels for high performance strain sensors. *Carbohydr Polym* 2019;211:322-8. DOI PubMed

33. Tian X, Yang P, Yi Y, et al. Self-healing and high stretchable polymer electrolytes based on ionic bonds with high conductivity for lithium batteries. *J Power Sources* 2020:450. DOI

34. Xu J, Chen J, Zhang Y, Liu T, Fu J. A fast room-temperature self-healing glassy polyurethane. *Angew Chem Int Ed Engl* 2021;60:7947-55. DOI PubMed

35. Ye S, Ma W, Shao W, Ejeromedoghene O, Fu G, Kang M. Gradient dynamic cross-linked photochromic multifunctional polyelectrolyte hydrogels for visual display and information storage application. *Polymer* 2022;243:124642. DOI

36. Song H, Sun Y, Zhu J, Xu J, Zhang C, Liu T. Hydrogen-bonded network enables polyelectrolyte complex hydrogels with high stretchability, excellent fatigue resistance and self-healability for human motion detection. *Composit Part B Eng* 2021;217:108901. DOI

37. Chen Q, Zhu L, Huang L, et al. Fracture of the physically cross-linked first network in hybrid double network hydrogels. *Macromolecules* 2014;47:2140-8. DOI

38. Chen Q, Wei D, Chen H, et al. Simultaneous enhancement of stiffness and toughness in hybrid double-network hydrogels via the first, physically linked network. *Macromolecules* 2015;48:8003-10. DOI

39. Sun TL, Kurokawa T, Kuroda S, et al. Physical hydrogels composed of polyampholytes demonstrate high toughness and viscoelasticity. *Nat Mater* 2013;12:932-7. DOI PubMed

40. Peng K, Wang W, Zhang J, et al. Preparation of chitosan/sodium alginate conductive hydrogels with high salt contents and their application in flexible supercapacitors. *Carbohydr Polym* 2022;278:118927. DOI PubMed

41. Zhao J, Chen Y, Yao Y, et al. Preparation of the polyelectrolyte complex hydrogel of biopolymers via a semi-dissolution acidification sol-gel transition method and its application in solid-state supercapacitors. *J Power Sources* 2018;378:603-9. DOI

42. Park S, Parida K, Lee PS. Deformable and transparent ionic and electronic conductors for soft energy devices. *Adv Energy Mater* 2017;7:1701369. DOI

43. Gong JP. Why are double network hydrogels so tough? *Soft Matter* 2010;6:2583-90. DOI

44. Wei S, Qu G, Luo G, et al. Scalable and automated fabrication of conductive tough-hydrogel microfibers with ultrastretchability, 3D printability, and stress sensitivity. *ACS Appl Mater Interfaces* 2018;10:11204-12. DOI PubMed

45. Yu HC, Zheng SY, Fang L, et al. Reversibly transforming a highly swollen polyelectrolyte hydrogel to an extremely tough one and its application as a tubular grasper. *Adv Mater* 2020;32:2005171. DOI PubMed

46. Yin H, Akasaki T, Lin ST, et al. Double network hydrogels from polyzwitterions: high mechanical strength and excellent anti-biofouling properties. *J Mater Chem B* 2013;1:3685-93. DOI PubMed

47. Huang KT, Hsieh PS, Dai LG, Huang CJ. Complete zwitterionic double network hydrogels with great toughness and resistance against foreign body reaction and thrombus. *J Mater Chem B* 2020;8:7390-02. DOI PubMed

48. Kim ES, Song DB, Choi KH, Lee JH, Suh DH, Choi WJ. Robust and recoverable dual cross-linking networks in pressure-sensitive adhesives. *J Polym Sci* 2020;58:3358-69. DOI

49. Cao J, Wang Y, He C, Kang Y, Zhou J. Ionically crosslinked chitosan/poly(acrylic acid) hydrogels with high strength, toughness and antifreezing capability. *Carbohydr Polym* 2020;242:116420. DOI PubMed

50. Han Z, Zhou P, Duan C. Extremely stretchable, stable and antibacterial double network organogels based on hydrogen bonding interaction. *Colloids Surfaces A Physicochem Eng Aspects* 2020;602:125065. DOI

51. Feng Z, Zuo H, Gao W, Ning N, Tian M, Zhang L. A robust, self-healable, and shape memory supramolecular hydrogel by multiple hydrogen bonding interactions. *Macromol Rapid Commun* 2018;39:1800138. DOI PubMed

52. Wei Z, Yang JH, Zhou J, et al. Self-healing gels based on constitutional dynamic chemistry and their potential applications. *Chem Soc Rev* 2014;43:8114-31. DOI PubMed

53.   Yuan T, Cui X, Liu X, Qu X, Sun J. Highly tough, stretchable, self-healing, and recyclable hydrogels reinforced by in situ-formed polyelectrolyte complex nanoparticles. *Macromolecules* 2019;52:3141-9. DOI

54.   Fang X, Sun J. One-step synthesis of healable weak-polyelectrolyte-based hydrogels with high mechanical strength, toughness, and excellent self-recovery. *ACS Macro Letters* 2019;8:500-5. DOI PubMed

55.   Wu J, Wu Z, Lu X, et al. Ultrastretchable and stable strain sensors based on antifreezing and self-healing ionic organohydrogels for human motion monitoring. *ACS Appl Mater Interfaces* 2019;11:9405-14. DOI PubMed

56.   Liu H, Wang X, Cao Y, et al. Freezing-tolerant, highly sensitive strain and pressure sensors assembled from ionic conductive hydrogels with dynamic cross-links. *ACS Appl Mater Interfaces* 2020;12:25334-44. DOI PubMed

57.   Zhou D, Chen F, Handschuh-Wang S, Gan T, Zhou X, Zhou X. Biomimetic extreme-temperature- and environment-adaptable hydrogels. *Chemphyschem* 2019;20:2139-54. DOI PubMed

58.   Cheng Y, Zang J, Zhao X, Wang H, Hu Y. Nanocellulose-enhanced organohydrogel with high-strength, conductivity, and anti-freezing properties for wearable strain sensors. *Carbohydr Polym* 2022;277:118872. DOI PubMed

59.   Morelle XP, Illeperuma WR, Tian K, Bai R, Suo Z, Vlassak JJ. Highly stretchable and tough hydrogels below water freezing temperature. *Adv Mater* 2018;30:1801541. DOI PubMed

60.   Zhao R, Yang H, Nie B, Hu L. Highly transparent, antifreezing and stretchable conductive organohydrogels for strain and pressure sensors. *Sci China Tech Sci* 2021;64:2532-40. DOI

61.   Dashnau JL, Nucci NV, Sharp KA, Vanderkooi JM. Hydrogen bonding and the cryoprotective properties of glycerol/water mixtures. *J Phys Chem B* 2006;110:13670-77. DOI PubMed

62.   Ying B, Chen RZ, Zuo R, Li J, Liu X. An anti-freezing, ambient-stable and highly stretchable ionic skin with strong surface adhesion for wearable sensing and soft robotics. *Adv Funct Mater* 2021;31:2104665. DOI

63.   Shao C, Wang M, Meng L, et al. Mussel-inspired cellulose nanocomposite tough hydrogels with synergistic self-healing, adhesive, and strain-sensitive properties. *Chem Mat* 2018;30:3110-21. DOI

64.   Gan D, Xing W, Jiang L, et al. Plant-inspired adhesive and tough hydrogel based on Ag-Lignin nanoparticles-triggered dynamic redox catechol chemistry. *Nat Commun* 2019;10:1487. DOI PubMed PMC

65.   Fu C, Lin J, Tang Z, et al. Design of asymmetric-adhesion lignin reinforced hydrogels with anti-interference for strain sensing and moist air induced electricity generator. *Int J Biol Macromol* 2022;201:104-10. DOI PubMed

66.   Wang J, Wang L, Wu C, et al. Antibacterial zwitterionic polyelectrolyte hydrogel adhesives with adhesion strength mediated by electrostatic mismatch. *ACS Appl Mater Interfaces* 2020;12:46816-26. DOI PubMed

67.   Akhtar MF, Hanif M, Ranjha NM. Methods of synthesis of hydrogels ... A review. *Saudi Pharm J* 2016;24:554-9. DOI PubMed PMC

68.   Hu X, Wang Y, Zhang L, Xu M. Formation of self-assembled polyelectrolyte complex hydrogel derived from salecan and chitosan for sustained release of Vitamin C. *Carbohydr Polym* 2020;234:115920. DOI PubMed

69.   Huang KT, Ishihara K, Huang CJ. Polyelectrolyte and antipolyelectrolyte effects for dual salt-responsive interpenetrating network hydrogels. *Biomacromolecules* 2019;20:3524-34. DOI PubMed

70.   Tong Z, Yang J, Lin L, et al. In situ synthesis of poly (gamma- glutamic acid)/alginate/AgNP composite microspheres with antibacterial and hemostatic properties. *Carbohydr Polym* 2019;221:21-8. DOI PubMed

71.   Maiz-Fernandez S, Perez-Alvarez L, Ruiz-Rubio L, Vilas-Vilela JL, Lanceros-Mendez S. Polysaccharide-based in situ self-healing hydrogels for tissue engineering applications. *Polymers (Basel)* 2020;12:2261. DOI PubMed PMC

72.   Li YQ, Zhu WB, Yu XG, et al. Multifunctional wearable device based on flexible and conductive carbon sponge/polydimethylsiloxane composite. *ACS Appl Mater Interfaces* 2016;8:33189-96. DOI PubMed

73.   Yao S, Zhu Y. Wearable multifunctional sensors using printed stretchable conductors made of silver nanowires. *Nanoscale* 2014;6:2345-52. DOI PubMed

74.   Zhang J, Chen L, Shen B, et al. Highly transparent, self-healing, injectable and self-adhesive chitosan/polyzwitterion-based double network hydrogel for potential 3D printing wearable strain sensor. *Mater Sci Eng C Mater Biol Appl* 2020;117:111298. DOI PubMed

75.   Sui X, Guo H, Cai C, et al. Ionic conductive hydrogels with long-lasting antifreezing, water retention and self-regeneration abilities. *Chem Eng J* 2021;419:129478. DOI

76.   Dos Santos CA, Seckler MM, Ingle AP, et al. Silver nanoparticles: therapeutic uses, toxicity, and safety issues. *J Pharm Sci* 2014;103:1931-44. DOI PubMed

77.   Teymourinia H, Salavati-Niasari M, Amiri O. Simple synthesis of Cu_2O/GQDs nanocomposite with different morphologies fabricated by tuning the synthesis parameters as novel antibacterial material. *Composit Part B Eng* 2019;172:785-94. DOI

78.   Chen T, Chen Y, Rehman HU, et al. Ultratough, self-healing, and tissue-adhesive hydrogel for wound dressing. *ACS Appl Mater Interfaces* 2018;10:33523-31. DOI PubMed

79.   Yang J, Chen Y, Zhao L, et al. Preparation of a chitosan/carboxymethyl chitosan/AgNPs polyelectrolyte composite physical hydrogel with self-healing ability, antibacterial properties, and good biosafety simultaneously, and its application as a wound dressing. *Composit Part B Eng* 2020;197:108139. DOI

80.   Hamidi M, Azadi A, Rafiei P. Hydrogel nanoparticles in drug delivery. *Adv Drug Deliv Rev* 2008;60:1638-49. DOI PubMed